

"comprehensive gas processor" that is a simple, compact, and both energy-efficient and cost-effective apparatus to be operated unattended in any gas field for on-situ processing of natural gas. Detailed explanations follow.

1. Review of my past research work on present invention

The new and useful improvements of my present invention over the prior arts as cited and the radical differences between said invention and prior arts are originated from past research work. A brief review follows.

Immediately followed my first invention in refrigeration gas dehydration (granted U.S. patent #5,664,426 in 1997), I began to study the application of such a process to the comprehensive processing of natural gas, i.e., simultaneously removing water and higher hydrocarbons within a single gas processor. ***The objective of said research is to develop an efficient, simple, compact and economic, skid-mounted mobile apparatus for on-situ recovery of higher hydrocarbons.***

Eventually said gas processor could replace the widely used commercial glycol dehydrators. It is an ambitious objective, and a real challenge as well. If successfully developed, such a comprehensive processor could produce both gas and light oil (i.e., C₂+) from every gas field. Light oil would then be produced in huge amount at much lower low cost. The current expensive and sophisticated cryogenic gas processing plants would no longer be a must. Such a prospect is particular attractive to developing countries having enormous natural gas resources but short of financial resources, such as the PRC. Extensive research work, therefore, has been vigorously carried out in my Beijing laboratory.

Four areas of gas processing technology have been studied in depth: (1) refrigeration/cryogenics, (2) absorption, (3) adsorption, and (4) membrane/diffusion. My research group reviewed and evaluated numerous patents, technical reports, and design documents. After first round of screening, the adsorption and membrane technologies were dropped because of their higher cost. We then focused on the remaining two more promising areas (1) and (2) that happened to cover these prior arts as cited. All available related patents were reviewed, analyzed, and evaluated during said research period, together with hundreds of other technical publications. The merits and shortcomings of these patents have been evaluated on the basis of their success or failure in commercialization since granted, in particular their respective competitiveness with State-of-the-art commercial products.

With extensive research work, I found none of the reviewed patents in either refrigeration or absorption process alone could serve my objective. Furthermore, I found the State-of-the-arts cryogenic separation process (patented by Campbell et al. and others) has obvious advantages over other processes for natural gas processing, and none of the other patents (including Mehra and Doerler's as cited) has been successful in competition during the past decades. It is also not possible simply to modify any prior arts as cited to serve my objective. After exhaustive research efforts, I worked out an innovative way to integrate two different processes into a "hybrid process" by ingeniously selecting two "second best players" (inhibitor and absorbent) and integrated them to play a superior "hybrid process", i.e., to perform an energy- and cost-effective triplet refrigeration-

dehydration-absorption process adequate for skid-mounted on-situ natural gas processing.

2. *Integration with Innovative Ideas*

Although my present invention is the outcome of an exhaustive research, not a kind of direct derivation from the prior arts as cited, a review of the radical differences between my said invention and Mehra and Doerler's patents as examples would be helpful to clarify the patentability of said invention.

Both US patents #4,421,535 by Mehra and #6,016,667 by Doerler have been reviewed and evaluated among others during said research work period, and both were found being unsuccessful in competition with State-of-the-art commercial products during the past decades.

Mehra's patent, based on using a highly selective DMPEG absorbent working under pipeline pressure and ambient temperature, seemed rather attractive for at first sight. However, in-depth study reveals the problems hidden in the follow-up absorbent regeneration process. In order to drive out the absorbed hydrocarbon gases, Mehra adopted 3-4 flush regeneration stages, i.e., from the pipeline pressure of 625 psia down to 400 psia, then 300 psia, then atmospheric, and finally a vacuum at 5 psia. However, in his patent, he did not explicitly address the negative consequences. In addition to the complexity of his sophisticated regeneration system, enormous power requirement for re-compressing the residual gas became a fatal drawback. (See Table1 below.) For this and other reasons, Mehra's patent failed to compete with the cryogenic process in commercial market during the whole term of said patent (1983-2000).

Table 1. A Comparison of Theoretical Power Consumption

For US paten # 4,421,535, data of Example 1 (column 11-13) is used. The gas inlet conditions are: gas flow rate--1MMSCFD, pressure—625 psia, temperature—120°F. For other data sources, see foot notes.

| Stream No.* | Description | Residual Gas Mols/hour | Flash Pressure | Compression Pressure | Est. Theoretical Power Consumption, kW |
|-------------------------|---------------------|------------------------|----------------|----------------------|--|
| 22 | Med. Pressure Flush | 8.69 | 400 | 625 | 1.1 |
| 32 | Low Pressure Flush | 6.30 | 300 | 625 | 1.6 |
| 72 | Vacuum Flash | 31.78 | 5 | 400 | 33.5 |
| 92 | Residual Methane | 13.02 | 400 | 625 | 1.7 |
| Sum | | | | | 37.9 |
| Cryogenic Process** | | | | | 31.6 |
| My present invention*** | | | | | 5.0 |

* Stream numbers refer to Fig. 1 and Table 1 of US patent #4,421,535. Because it is unrealistic to use a single stage compressor after the vacuum flush to compress the gas from 5 psia to 400 psia, a two stage compressor with inter-cooling is assumed in the estimation.

** Refer to US patent #5,983,664, Campbell et al., 1999, Example 1, Table 1; the power consumption is converted to theoretical power consumption value for 1MMSCFD.

*** Power consumption of the refrigerator, converted to theoretical value for treatment of 1MMSCFD.

Doerler's patent, based on refrigeration dehydration and de-gasoline (not full recovery) process with methanol injection as hydrate inhibitor, is not a new concept in natural industry. Although Doerler got his US patent only recently in 2000 (his another related patent [with others] was granted as US patent #5,868,004 in 1999), an almost identical process in US had been thoroughly studied (both experimentally and analytically), designed and published by R.B. Nielson and R.W. Bucklin under the title "Why Not Use Methanol for Hydrate Control?" in *Hydrocarbon Processing*, April 1983, pp.71-78, about 17 years before Doerler (happened to be in the same year of Mehra's patent). Doerler's main contribution to the old methane-controlled dehydration process lies in his improvements of methanol recovery process. However, even with his sophisticated three-stage recovery system, significant quantity of methanol makeup is still required—16kg/hr or 384kg/day according to his estimation (see column 7 of his patent). The methane loss problem has not been fully eliminated. It is not surprising that, therefore, during the past two decades since Nielson and Bucklin's publication, no methanol-controlled dehydrator was successful in competing with the commercial glycol dehydrator in the market. In addition, simple refrigeration could not be accounted for an efficient C₂₊ recovery process because of the poor recovery rate for C₂ and C₃. It is, therefore, inadequate for on-situ gas processing. In fact, similar efforts on developing methane-controlled dehydrator in the PRC have been carried out recently by other institutions (Dalian and Changqing) without success in commercial market.

Further more, since my main objective is to develop an on-situ apparatus for unattended operations in gas fields, the complexity of the above systems is also an obvious impassable obstacle. Mehra's system comprises 3 contactors, 3-4 flush tanks, 4 gas compressors, 5 heat exchangers, 2 re-boilers, and 4 pumps, with a refrigerator required to cool the vacuum flushed gas to 20°F not shown in his cover drawing-- a total of 22-23 pieces of equipment. Doerler's system comprises 3 contactors, 3 heat exchangers, 1 gas compressor and 1 pump, with a re-boiler and a refrigerator not shown in his cover drawing—a total of 10 pieces of equipment. No person having ordinary skill could ever imagine how to integrate these two complex systems with a total of 31-32 pieces of equipment (with a common refrigerator) into a simple on-situ skid-mounted mobile apparatus as the commercial glycol dehydrators, with only 8 pieces of equipment as shown in FIGs 1 and 2 of my patent application.

It is impossible to add two negative numbers to get a positive number in mathematics. It is also impossible to incorporate two unsuccessful technologies into a successful technology in commercial market. Innovative ideas are required to conceive how to integrate two unsuccessful processes into a success one.

According to my philosophy, when developing an innovative new technology, the key player therein should be evaluated on a *system-engineering* basis, i.e., not only the merits of said *player per se*, but that of *its arena*—the entire system required for said performance. It seemed to me that both Mehra and Doerler proceeded the other way. They selected their key players (absorbent or inhibitor) by the *performance per se*, and did not evaluate the players' respective *regeneration*

systems. As a consequence, although they did select attractive well-known absorbent or inhibitor of superior performance, yet the hidden problems in their respective regenerator systems eventually led to commercial failure.

More specifically, Mehra selected his player on the basis of superiority of individual absorbent's performance. As addressed in his patent, Mehra selected DMPEG because of (1) its superior selectivity ($\alpha=6.4$ at ambient temperature for methane vs. ethane) and relatively higher hydrocarbon gas solubility (1SCF/gal) over other synthetic absorbents such as NMP and DMP; (2) its capability of remove water and higher hydrocarbons simultaneously; and (3) its favorable working environments, i.e., at ambient temperature and pipeline pressure. These sounded perfect, however, DMPEG's merits just stopped here. What really mattered in the commercialization process was the system performance. Mehra neglected the shortcomings of his follow-up regeneration system. The demerits of complexity of a multi-staged flushing system and the resulted enormous power consumption required for re-compressing the residual gas offset most of DMPEG's merits. The neglected effects of poor system performance accounted for the failure of Mehra's patent in competition with Campbell's cryogenic technology.

Doerler's patent reflected the same problem. Doerler selected a superior player—methanol as inhibitor, based on traditional thoughts. Methanol is a volatile substance easily to be evaporated and uniformly distributed in the gas to be processed. In view of the drawbacks of the methanol-controlled dehydration technology proposed by Nielson and Bucklin in 1983, Doerler tried to eliminate the methanol loss. Doerler was not aware of the root-cause originated from the wrong player *per se*. Methanol as an inhibitor is too active to be fully recovered. Methanol not only has high vapor pressure but also very high solubility in both water and liquid hydrocarbons. As a consequence, it has to be recovered from all the fluids involved in the process, i.e., the gas, the hydrocarbon liquids, and the water. In spite of the sophistic design in Doerler's patent, the loss of methanol is still non-trivial—16kg/hour or 384kg/day—an amount not acceptable to most applications, in particular to on-situ field operations.

Based on my philosophy, I chose to attack the problem alternatively—with a *system engineering* approach. I selected a hybrid system comprises *two “second best” players*, each performs their specific function in a much simpler system, and then *integrate two “second best players” into a superior “hibrid player”* to perform the challenging function of on-situ gas processing. However, said integration process needs more innovative ideas.

First, for the refrigeration-dehydration function, I choose a different kind of player—an aqueous solution of low volatile inhibitors such as ethylene glycol or CaCl_2 , generally considered inferior than methanol for preventing hydrates in gas dehydration. These low volatile inhibitors, however, also have low solubility in hydrocarbon liquids. The regeneration system is extreme simple with warm air stripping. A major drawback of these “second best” inhibitors is the difficulty to keep them always uniformly distributed in the gas stream through an irregular flow path inside a heat exchanger. An ingenious approach has been devised to solve this problem. In contrast to common

practice of distributing the inhibitor uniformly into the gas, I choose to directly contact the gas with the chilled aqueous inhibitor solution in an extraction-tower typed "heat exchanger". While the gas is cooled when flowing through the tower, the water vapor is condensed directly to the surfaces of the well-dispersed inhibitor solution and dissolved into the solution. Gas hydrate formation is thus eliminated. A significant part of the higher hydrocarbon gases is also condensed and recovered in this process as a by-product.

Secondly, to fully recover the remaining higher hydrocarbons (mainly ethane, and a smaller portion of propane) from the refrigerated gas stream, an easy-regenerated absorbent (e.g., heavy oil) with very high hydrocarbon gases solubility is selected. Its lower selectivity compared to DMPEG at ambient temperature is improved with lowering the operational temperature. For instance, the alpha of heavy oil increases from about 4 at 120°F to 6.4 at -30°F. Because the incoming gas is already cooled in previous dehydration stage, the major drawback of low-temperature absorption process--energy consumption--is reduced to a minimum.

The innovative idea for integration of *two "second best" players* to play a superior "*hybrid processor*" resulted in surprisingly simplicity of the systems proposed in my invention. Refer to FIGs. 1 and 2 of said invention, each embodiment comprises only 8 pieces of equipment, in contrast to a total of 31-32 pieces of equipment in a combined Mehra-Doerler's system. The simple, compact gas processor thus resulted could easily be put on a skid to perform the on-situ for gas processing and replace ordinary glycol dehydrators.

3. Summary of innovative features of the comprehensive gas processor

The innovative features of the comprehensive gas processor comprising:

(1) An refrigeration-dehydration process radically different from Doerler's process in a) the type of inhibitor selected, b) the inhibitor application mode (not injected into the gas, but dissolved into the cooling medium), c) the direct contact heat transfer mode and d) much simplified regeneration process. In present invention, the inlet gas is cooled in direct contact with a counter-flowing stream of well dispersed refrigerated aqueous solution (cooling-medium) of a non- or low-volatile hydrate inhibitor (e.g., CaCl₂ or ethylene glycol) with very low (or zero) solubility in hydrocarbon liquid, thus eliminate the needs (as in Doerler's process) to recover said inhibitor from the processed gas stream and the hydrocarbon liquid.

(2) A simplified low-temperature absorption process radically different from Mehra's ambient temperature DMPEG absorption process in: a) the type of absorbent selected, b) the low-temperature working environment, c) the one-step high pressure regeneration process without multiple-stage flush process, d) much simplified regeneration system and e) enormous power savings. In present invention, the cold gas (e.g., at -30°C) leaving the dehydration section is brought to contact with a counter-flowing stream of well-dispersed low-temperature absorbent with very high hydrocarbon solubility (e.g., heavy oil). The regeneration of said absorbent is carried out under high pressure in a single fractional distiller with very little pressure loss. No re-compression of residual gas is required.

(3) Very low power consumption. Because of the lack of power supply in most gas fields, the power consumption in-situ processing of natural gas should be minimized. The present invention does not require recompression of residual gas. The power requirement of refrigeration is greatly reduced with a highly efficient direct contact heat exchanger and heat recuperation. A comparison of the power consumption (see above Table 1) shows about 80% power saving of present invention to either the State-of-the-arts cryogenic separation plants or Mehra's process.

(4) Very low inhibitor consumption. For on-situ gas processor units, frequent makeup of the inhibitor is very inconvenient and undesirable. According to Example 2 given in Doerler's patent ('667 column 7), a 23.25 ton/hr (about 25 MMSCFD) dehydrator requires 16 kg/hr or 384kg/day makeup of methanol even with his sophisticated regeneration system (FIG.2 of said patent). On the contrary, in my said invention, because non- or low-volatile inhibitor is used, the loss of inhibitor is less than 1% of Doerler's. Such a negligible inhibitor consumption makes unattended on-situ operations possible.

(5) Very simple, compact inhibitor regenerator. In Doerler's patent, the methanol inhibitor needs to be recovered from wastewater, processed gas, and light oil liquid. In my present invention, only a small side-stream of the aqueous inhibitor solution (about 100 lb/hr) need to be regenerated. Because the high water content in the solution (40-70% Wt.), the flow rate across the inhibitor regenerator is in general less than 10% of the glycol flow through the re-boiler in commercial glycol dehydrator of the same gas dehydration capacity.

(6) Very simple, compact fractional distiller. Very high solubility absorbent is used in present invention (e.g., unlimited solubility for heavy oil vs. 1SCF/gal for DMPEG in Mehra's patent). In addition, substantial fraction of higher hydrocarbon content (particularly C₃+) in the gas has been removed before the refrigerated gas enters the absorption section. As a consequence, the quantity of absorbent to be treated in present invention is less than 10% of that in Mehra's patent. The regeneration is performed under pressure with traditional fractional distillation process. No flush de-gasing of the lean absorbent and re-compression of the residual gas are required.

In summary, the innovative hybrid process proposed in my present invention is the outcome of the extensive research during past years. The comprehensive gas processor using hybrid process is simple, compact, and efficient. The comprehensive gas processor features new and useful improvements over prior arts, and is capable to perform on-situ procession in natural gas fields. *All the above-mentioned new and useful improvements over prior arts are included in the Revised Claims below.*

B. On Revisions of Other Claims

The other claims are revised as dependent claims to further specify the innovative features summarized in Claim 1.

The revised Claims 2 describes an alternative application of Claim 1.

The revised Claims 3-5 details the innovative features of the inhibitor and absorbent cited in Claim 1.

The revised Claim 6 specifies the conditions under which a gas expansion device is justified to replace the refrigerator of Claim 1. The threshold pressure value 5.0 MPa (a little above the critical pressure of methane) is based on another important findings in my said research. I found that, when inlet gas pressure above a certain threshold value, in case the gas pressure at exit of the gas expander-compressor is below the required delivery pipeline pressure, the supplementary power required to compress the gas to the pipeline will be equal to or less than the power required by the refrigerator of Claim 1. Then the replacement of said refrigerator with a gas expansion device could be justified.

The revised Claim 7 details the innovative triple-sectional free-piston expander-compressor-booster that meet the conditions of the revised Claim 6.

(Revised Claims in following pages)